



Structural stability and elastic properties of prototypical covalent organic frameworks

Wei Zhou^{a,b,*}, Hui Wu^{a,b}, Taner Yildirim^{a,c}

^a NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, United States

^b Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, United States

^c Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104-6272, United States

ARTICLE INFO

Article history:

Received 9 August 2010

In final form 11 September 2010

Available online 17 September 2010

ABSTRACT

We report the first investigation of the structural stabilities and elastic properties of covalent organic frameworks (COFs), a new class of porous crystalline materials. Representative 2D COFs were found to prefer shifted AA stacking, somewhat similar to graphite. The shear moduli of 2D COFs are exceedingly small, suggesting that the layer–layer coupling in 2D COFs is rather weak, and stacking faults may widely exist. Representative 3D COFs were found to exhibit relatively low elastic stiffness overall. In particular, COF-108, the least dense crystal known, exhibits rather low bulk and shear moduli. Our findings provide important structural and physical details to be considered in the further development of COF materials.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Covalent organic frameworks (COFs), consisting of strong covalent bonds (B–O, C–O, C–C, etc.) connected by organic linkers, are a new class of porous, crystalline, coordination framework compounds [1–3]. Their high surface areas (up to ~ 5000 m²/g), large free volumes, and low densities (as low as 0.17 g/cm^{−3}) make these materials promising for a variety of applications. In particular, they are considered as new candidates for gas storage [1–6]. Since the initial report [1] in 2005, dozens of new COF compounds have been synthesized, mostly by Yaghi's group. COFs can be categorized into two groups: Two-dimensional (2D) COFs with layered structures and three-dimensional (3D) COFs with network structures. As for other porous coordination framework materials [e.g., zeolites, metal–organic frameworks (MOFs), etc.], structural stability is an important issue for COFs, since from a thermodynamics viewpoint, microporous structures are all metastable with respect to dense structures. The pores of as-synthesized COFs often contain chemical solvents or precursors used during the solvothermal synthesis processes [1–3]. How to activate the material (i.e., remove the guest molecules) without collapsing the framework pore structure represents an additional complication. Indeed, only a few members in the COF family have been successfully activated thus far [5]. For COFs that were experimentally found difficult to activate, one may wonder if the structures would maintain integrity at all after removing the guest molecules.

In this study, we try to address this fundamental issue of COF materials by theoretically evaluating the structural stabilities and elastic properties of four representative COF compounds: COF-1 (C₃H₂BO), COF-5 (C₉H₄BO₂), COF-102 (C₂₅H₁₆B₄O₄) and COF-108 (C₄₉H₂₄B₄O₈). The first two are prototypical 2D COFs while the latter two are prototypical 3D COFs.

2. Computational method

To perform our calculations, we used the self-consistent Density Functional based Tight Binding (DFTB) method [7], as implemented in the DFTB+ package [8]. The DFTB method is based on a second-order expansion of the Kohn–Sham total energy in Density-Functional Theory (DFT) with respect to charge density fluctuations [7]. It combines the reliability of DFT and the efficiency of the tight binding approach. The computational cost needed by a DFTB calculation is typically two orders of magnitude smaller than a corresponding DFT calculation, making it highly attractive for calculations on extended framework structures, in particular those with large unit cells that contain several hundreds or even thousands of atoms. The ‘matsci’ parameter set, which includes Slater–Koster files developed specifically for ‘B–O–C–H frameworks’, was adopted in our calculations [9]. For 2D COFs, correction for dispersive interactions based a Slater–Kirkwood type model [10] was also included in the calculation, which was found to be critical for the proper treatment of the interlayer van der Waals (vdW) interactions (same calculation without vdW correction leads to unphysical, large interlayer distances).

Since this was the first time that the DFTB approach was applied to COF calculations, it was important to test how well the adopted

* Corresponding author at: NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, United States.

E-mail address: wzhou@nist.gov (W. Zhou).

parameter set works. For this purpose, selected calculations were also performed using the higher level DFT method. We used the Quantum ESPRESSO package [11], Vanderbilt-type ultrasoft pseudopotential with Perdew–Burke–Ernzerh (PBE) exchange correlation. A suitable k -point mesh ($2 \times 2 \times 5$ for 2D COFs and $1 \times 1 \times 1$ for 3D COFs) and a 410 eV cutoff energy were found enough for the total energy to converge within 0.5 meV per atom. For 2D COFs, the dispersive interaction was also corrected using a semi-empirical method [12]. As shown below, whenever possible, we directly compared the DFTB results with the more accurate DFT results and/or experimental data. This gave us necessary confidence in the accuracy of our DFTB calculations for COFs.

3. Results and discussion

3.1. 2D COFs: COF-1 and COF-5

As-synthesized COF-1 (containing residual mesitylene guest molecules) was reported to have a 2D structure with staggered AB layers ($P63/mmc$) [1]. The interlayer distance derived from X-ray diffraction is ~ 3.33 Å. After activation, the compound was found to remain crystalline, but with some shifting of the layers [1]. In our calculations, we therefore considered two possible structure models (see the inset of Figure 1) for the fully activated, guest-free COF-1 compound: a structure with layers with AB stacking ($P63/mmc$, same as as-synthesized COF-1) and a structure with layers with AA stacking ($P6/mmm$). We calculated the energy as a function of interlayer spacing for both structures, with the in-plane lattice parameters fixed at the experimental values. The results are shown in Figure 1. Clearly, the AB-stacked structure with an interlayer distance of ~ 3.33 Å would not remain stable and will shrink along the c -axis direction. The AA-stacked structure has a slightly lower energy [by ~ 140 meV per chemical formula of $6(C_3H_2BO)$] than the AB-stacked structure in equilibrium, suggesting that an AA-stacked structure is preferred.

Our full optimization of the COF-1 structure with AA stacking gave the following equilibrium lattice constants: $a = b = 14.90$ Å, $c = 3.24$ Å (at zero temperature and pressure), which are fairly close to those of as-synthesized COF-1 obtained experimentally at RT

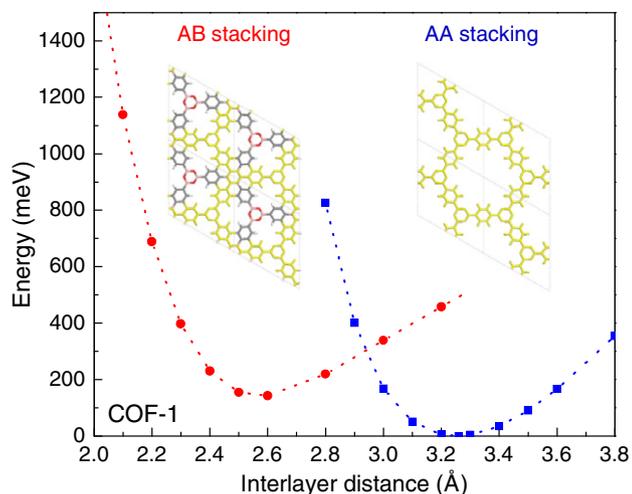


Figure 1. Calculated total energies of the COF-1 structures with AB stacking (red) and AA stacking (blue) as a function of interlayer spacing. The energy is normalized to the chemical formula of $6(C_3H_2BO)$, and shifted so that the equilibrium AA-stacked structure has zero energy. Structures shown in inset are $2 \times 2 \times 1$ supercells, in the $[001]$ direction, with top layer highlighted for clarity. Color scheme of atoms: B, pink; C, gray; O, red; and H, white. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

($a = b = 15.42$ Å, $c = 3.33$ Å). (In comparison, DFT–PBE calculations give similar equilibrium lattice constants $a = b = 15.50$ Å, $c = 3.38$ Å.) To test if the AA-stacked structure is indeed a stable structure for COF-1, we directly calculated its elastic properties. For a hexagonal crystal, there are five independent elastic coefficients: c_{11} , c_{12} , c_{13} , c_{33} and c_{44} . Therefore, we applied five symmetry-independent strains: $(\gamma, \gamma, 0, 0, 0, 0)$, $(\gamma, -\gamma, 0, 0, 0, 0)$, $(0, 0, \gamma, 0, 0, 0)$, $(0, 0, 0, 0, 2\gamma, 0)$ and $(\gamma, \gamma, \gamma, 0, 0, 0)$ to extract the five unknowns [13,14]. We carefully chose the value of γ in the general range of $[-0.05, +0.05]$ to make sure that the energy difference induced by the strain is significantly above the calculation error, while at the same time the distortion of the crystal is small enough so that it is within the linear elastic region. Atomic positions were fully optimized for all strained structures. From the least-squares fit of the total energy vs. strain data [15] (not shown), we found that $c_{11} = 143.7$ GPa, $c_{12} = 123.5$ GPa, $c_{13} = -0.1$ GPa, $c_{33} = 11.8$ GPa and $c_{44} = -0.4$ GPa. In a system of hexagonal elastic symmetry, the stability requirements are: $c_{11} > |c_{12}|$, $c_{33}(c_{11} + 2c_{12}) > 2(c_{13})^2$, $c_{11}c_{33} > (c_{13})^2$ and $c_{44} > 0$. Clearly, the negative value of c_{44} suggests that the crystal cell is not stable under in-plane shear.

Guided by this finding, we further investigated how the system energy changes when we slide two adjacent layers against each other by scanning a fine mesh of shifts in both in-plane directions. Interestingly, small shifting (within 1 Å) between the two adjacent layers was indeed found to further decrease the total energy of the system. There actually exist several possible ways of layer–layer arrangements that deviate slightly from the straight AA-stacked structure, and were metastable [we hereafter collectively refer to these structural possibilities as ‘shifted AA-stacked structures’, with two representative examples (a ‘tilted AA-stacked structure’ and an ‘AA’-stacked structure’) shown in Figure 2a and b]. This finding is not only consistent with the negative value of c_{44} obtained for the straight AA-stacked structure, but also in excellent agreement with previous experimental observation: the X-ray diffraction pattern of the activated COF-1 sample differs significantly from that of as-synthesized COF-1 [1], and we noticed that it actually closely resembles the simulated pattern of a shifted AA-stacked structure. The existence of several variations of layer–layer stacking with similar energies also suggests that the actual COF-1 material would contain many local disorders (stacking faults, etc.), and exhibit an overall modest crystallinity. This is again in accord with the broad diffraction peaks observed experimentally for COF-1, as reported previously [1].

Next we discuss COF-5. As-synthesized COF-5 was reported to possess a 2D structure with eclipsed layers in straight AA stacking ($P6/mmm$) [2]. Activation was found not to change the stacking arrangement of the layers [2]. Our full optimization of a guest-free COF-5 structure with straight AA stacking gave the following equilibrium lattice constants: $a = b = 30.05$ Å, $c = 3.30$ Å, which are again fairly close to those of as-synthesized COF-5 obtained experimentally ($a = b = 29.70$ Å, $c = 3.46$ Å). (In comparison, DFT–PBE calculations give similar equilibrium lattice constants $a = b = 29.85$ Å, $c = 3.49$ Å.) Similar to COF-1, the elastic constant calculation produces a negative value for $c_{44} = -0.2$ GPa, suggesting cell instability against in-plane shear. A small shifting (within 1 Å) between two adjacent layers was also found to be able to further decrease the total energy, and stabilize the system. Figure 2c and d shows two typical examples of such shifted AA layer–layer arrangements. Same as COF-1, the actual COF-5 material may be rich in stacking faults, with modest long-range order.

The preference of shifted AA stacking over straight AA stacking is very likely due to a system requirement of optimal stacking of π -orbitals between two adjacent COF layers, somewhat similar to the case of graphite. Indeed, the stacking of the aromatic rings of the organic linker in both COF-1 and COF-5 is essentially the same as the stacking of graphene layers in graphite (see Figure 2). Since

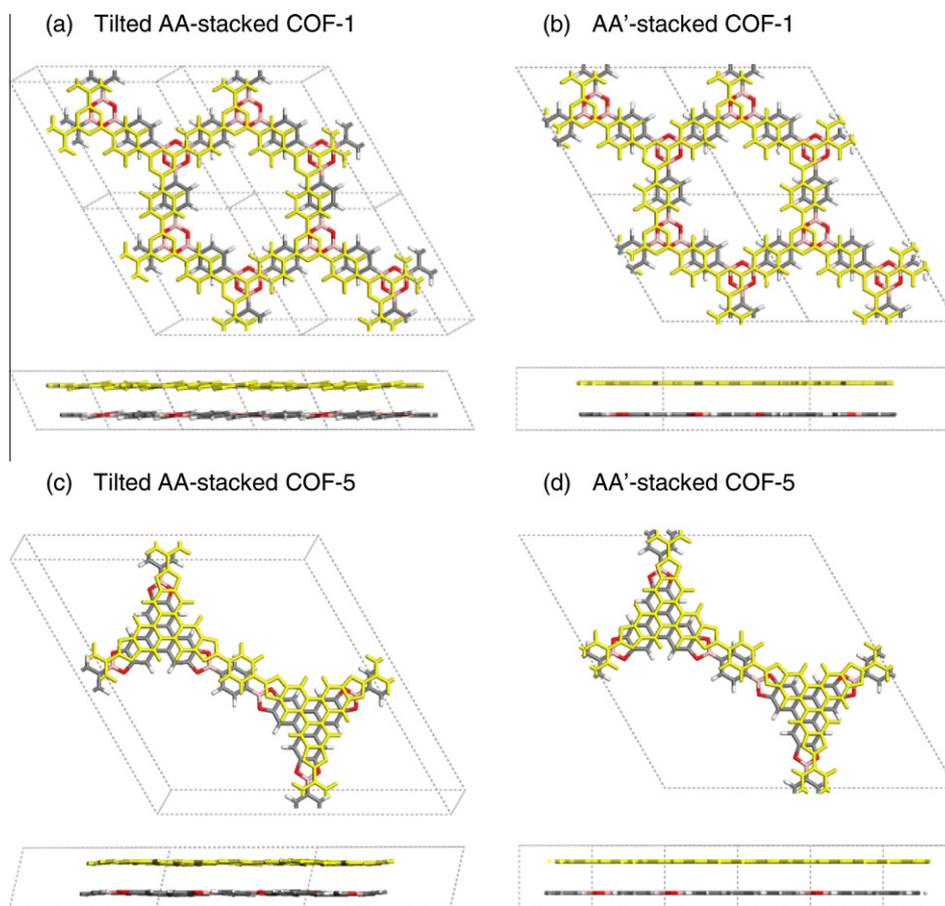


Figure 2. Structures of shifted AA-stacked COF-1 and COF-5. Both top view and side view are shown for each structure. Instead of a straight AA stacking, the 2D COF layers prefer a way of stacking similar to that in graphite, presumably with maximized π - π interaction between the aromatic rings in two adjacent layers. For clarity, top layers are highlighted. Color scheme of atoms are the same as in Figure 1. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

the energy gain of such stacking is not trivial, we believe that what we found here might be a general result for 2D COFs, particularly for those with organic linkers containing a large number of phenyl rings, i.e., other 2D COFs (e.g., COF-6, COF-8, COF-10, etc.) are very likely to undergo shifted AA stacking with abundant stacking disorder.

Due to the lowered symmetry ($C2/m$, monoclinic lattice for the tilted AA-stacked structure; $P21/m$, monoclinic lattice for the AA'-stacked structure) and many other possible stacking variations, we did not perform full elastic constant calculations on the shifted AA-stacked structures. A calculation of c_{44} for the two representative AA'-stacked COF-1 and COF-5 structures gave small positive values, 0.5 and 0.1 GPa, respectively. Thus, the shifted AA-stacked crystal cells are likely stable, although the energy cost of layer-layer sliding would still be rather small. We emphasize that this low shear modulus is not totally unexpected. 2D COFs in many ways resemble 'graphitic materials with pores', with weak layer-layer coupling. Indeed, graphite is known to have a low shear modulus of ~ 4 GPa, and that of some highly defected graphite (e.g., pyrographite or highly oriented pyrolytic graphite) could be as low as 0.2 GPa [16].

3.2. 3D COFs: COF-102 and COF-108

Three-dimensional COFs, in general, exhibit much higher crystallinity and better defined structures than 2D COFs. This naturally makes our calculation and discussion much more straightforward. COF-102 and COF-108 both have cubic crystal symmetry, with

space groups: $I\bar{4}3d$ and $P43m$, respectively (see Figure 3) [2]. The crystal densities of these two compounds are extraordinarily low (0.41 and 0.17 g/cm³, respectively), and COF-108 is believed to be the least dense crystal known [2]. The high porosities and ultra-low densities make it highly interesting to study their crystal cell stabilities and elastic properties.

Full optimization of the COF-102 and COF-108 structure results in equilibrium lattice constants $a = 26.86$ and 28.10 Å, respectively, fairly close to the experimental values [2] of 27.18 and 28.40 Å. (In comparison, DFT-PBE calculations give similar equilibrium lattice constants $a = 27.20$ and 28.33 Å, respectively.) We then calculated the elastic moduli of the two crystals and examined whether the resulted elastic constants satisfied the criteria for crystal stability. For a cubic crystal, there are three independent elastic coefficients c_{11} , c_{12} and c_{44} . Therefore, we applied three symmetry-independent strains: $[\gamma, \gamma, (1 + \gamma)^{-2} - 1, 0, 0, 0]$, $[\gamma, \gamma, \gamma, 0, 0, 0]$ and $[0, 0, \gamma^2(4 - \gamma^2)^{-1}, 0, 0, \gamma]$ to extract the three unknowns [17]. The first strain is a volume-conserving tetragonal deformation along the c -axis; the second one refers to uniform hydrostatic pressure; the third one corresponds to a volume-conserving orthorhombic shear. Again, we carefully choose γ to ensure the calculation accuracy and the validity of the harmonic approximation. All strained structures were fully optimized with respect to atomic positions. The least-squares fit of the total energy vs. strain data are shown in Figure 4 for both COFs. The quality of the data fit is reasonable. We found that $c_{11} = 22.9$ GPa, $c_{12} = 21.0$ GPa and $c_{44} = 1.5$ GPa for COF-102, and $c_{11} = 5.5$ GPa, $c_{12} = 4.5$ GPa and $c_{44} = 1.0$ GPa for COF-108. For a cubic crystal, the Voigt Bulk Modulus

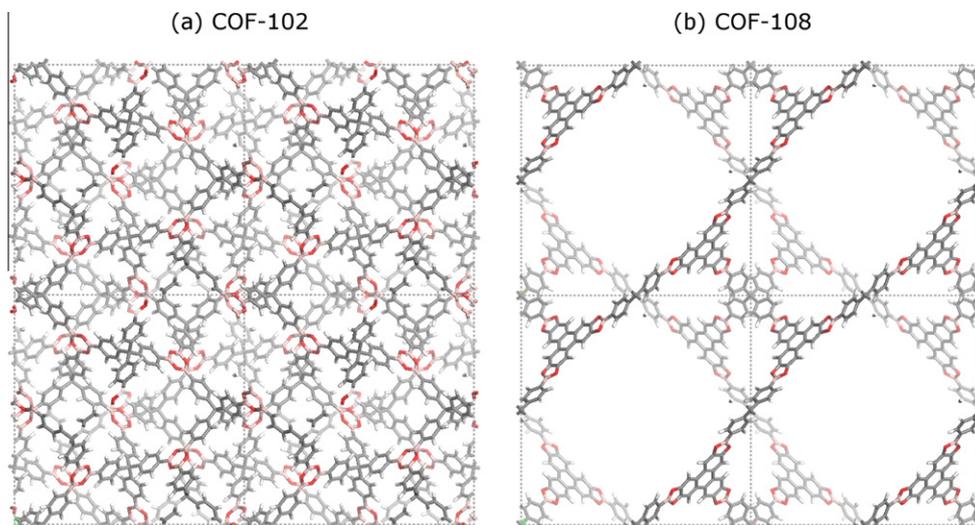


Figure 3. Crystal structures of (a) COF-102 and (b) COF-108, both of which are 3D COFs. $2 \times 2 \times 1$ supercells are shown, in the $[001]$ direction. Color scheme of atoms are the same as in Figure 1. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

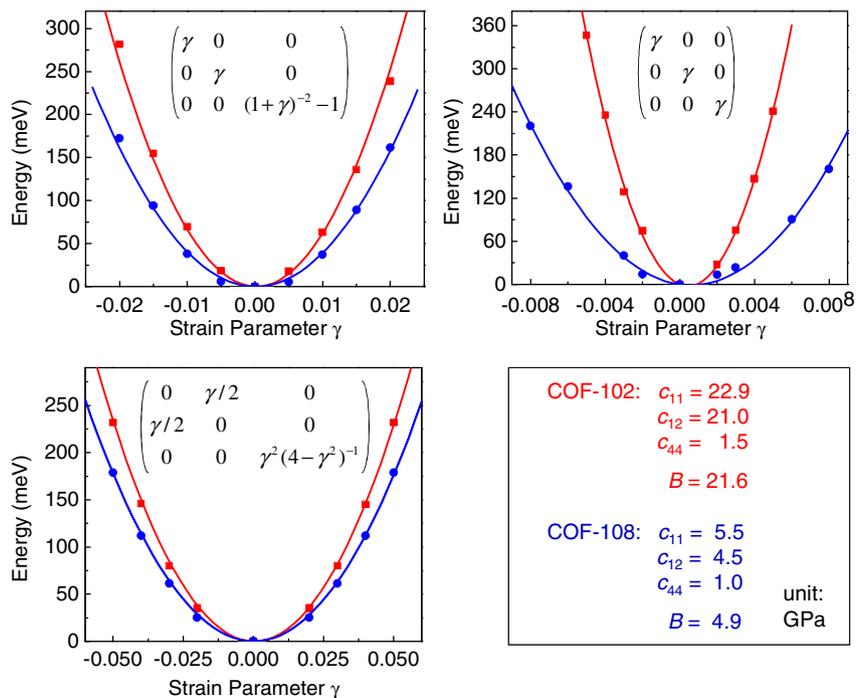


Figure 4. Least-squares fit of the total energy data vs. strain parameters. Data for COF-102 and COF-108 are shown in red and blue, respectively. The dots are from the DFTB calculations and the solid lines are the least-square fit. The deformation matrices for each distortion are also shown. The three cubic elastic constants along with the bulk modulus are summarized in the right-bottom panel. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

$B = (c_{11} + 2c_{12})/3$, thus we obtained 21.6 and 4.9 GPa for COF-102 and COF-108, respectively. In terms of crystal stability, the calculated elastic moduli of both COFs clearly satisfy the stability criteria for a cubic system (i.e., $c_{11} > c_{12}$, $c_{11} + 2c_{12} > 0$ and $c_{44} > 0$).

We note that the elastic moduli in both COFs are relatively small; in particular, the shear modulus c_{44} is quite small, only slightly larger than those of 2D COFs. However, these are comparable to those of many other 3D porous coordination framework materials. For example, metal-organic framework-5 (MOF-5, a well-known, benchmark, porous framework compound) exhibits $c_{11} = 25.5$ GPa, $c_{12} = 12.2$ GPa and $c_{44} = 0.9$ GPa according to our DFTB calculations (which agree reasonably well with our previ-

ously reported results [18] derived from higher level DFT calculations: $c_{11} = 29.4$ GPa, $c_{12} = 12.6$ GPa and $c_{44} = 1.2$ GPa). In terms of overall mechanical strength, 3D COFs also compare well with many well-known polymeric materials (such as high-density polyethylene).

Comparing COF-102 and COF-108, it appears that 3D COFs with higher porosity and lower density may generally have weaker mechanical strength, as one would expect. COF-108, the least dense crystal known, has a quite low shear modulus, coupled with a rather low bulk modulus, putting it in a dangerous zone very close to structural instability. Interestingly, we note that although successful experimental activation of COF-102 has been reported

in the literature, the same is not true for COF-108. Thus, it is not clear whether the COF-108 structure would retain its high crystallinity upon the removal of guest molecules. We expect that a molecular dynamic simulation at finite temperature may provide some insight on this topic, and such a task is currently ongoing in our group.

4. Summary

In summary, we have investigated the structural stability and elastic properties of four prototypical COFs. 2D COFs were found to prefer a shifted AA interlayer stacking, different from previously generally-believed straight AA or AB stacking. The shear modulus of 2D COFs are very low, comparable to that of highly defective graphite. 3D COFs were also found to possess very modest bulk and shear moduli, similar to typical MOFs. COF-108, in particular, is very close to structural collapse due to its high porosity and low elastic stiffness. These fundamental structural and physical characteristics of COFs provide important information for the further development of their potential applications.

Acknowledgment

This work was partially supported by the US Department of Energy through BES Grant No. DE-FG02-08ER46522 (T.Y.).

References

- [1] A.P. Côté, A.I. Benin, N.W. Ockwig, M. O'Keeffe, A.J. Matzger, O.M. Yaghi, *Science* 310 (2005) 1166.
- [2] H.M. El-Kaderi, J.R. Hunt, J.L. Mendoza-Cortés, A.P. Côté, R.E. Taylor, M. O'Keeffe, O.M. Yaghi, *Science* 316 (2007) 268.
- [3] (a) R.W. Tilford, W.R. Gemmil, H. zur Loye, J.L. Lavigne, *Chem. Mater.* 18 (2006) 5296;
(b) A.P. Côté, H.M. El-Kaderi, H. Furukawa, J.R. Hunt, O.M. Yaghi, *J. Am. Chem. Soc.* 129 (2007) 12914;
(c) W. Shun, G. Jia, K. Jangbae, I. Hyotcherl, J. Donglin, *Angew. Chem., Int. Ed.* 47 (2008) 8826;
(d) P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem., Int. Ed.* 47 (2008) 3450;
(e) F.J. Uribe-Romo, J.R. Hunt, H. Furukawa, C. Klck, M. O'Keeffe, O.M. Yaghi, *J. Am. Chem. Soc.* 131 (2009) 45701.
- [4] (a) G. Garberoglio, *Langmuir* 23 (2007) 12154;
(b) E. Klontzas, E. Tylianakis, G.E. Froudakis, *J. Phys. Chem. C* 112 (2008) 9095.
- [5] S.S. Han, H. Furukawa, O.M. Yaghi, W.A. Goddard III, *J. Am. Chem. Soc.* 130 (2008) 11580.
- [6] (a) H. Furukawa, O.M. Yaghi, *J. Am. Chem. Soc.* 131 (2009) 8875;
(b) C.J. Doonan, D.J. Tranchemontagne, T.G. Glover, J.R. Hunt, O.M. Yaghi, *Nat. Chem.* 2 (2010) 235.
- [7] T. Frauenheim et al., *J. Phys.: Condens. Matter* 14 (2002) 3015.
- [8] <http://www.dftb-plus.info>.
- [9] <http://www.dftb.org/parameters/download/matsci/matsci02/>.
- [10] M. Elstner, P. Hobza, T. Frauenheim, S. Suhai, E. Kaxiras, *J. Chem. Phys.* 114 (2001) 5149.
- [11] P. Giannozzi et al., *J. Phys.: Condens. Matter* 21 (2009) 395502.
- [12] V. Barone, M. Casarin, D. Forrer, M. Pavone, M. Sambri, A. Vittadini, *J. Comput. Chem.* 30 (2009) 934.
- [13] (a) L. Fast, J.M. Wills, B. Johansson, O. Eriksson, *Phys. Rev. B* 51 (1995) 17431;
(b) W. Zhou, H. Wu, T. Yildirim, *Phys. Rev. B* 76 (2007) 184113.
- [14] Note that here $(s_1, s_2, s_3, s_4, s_5, s_6)$ was conveniently used to represent a strain tensor of $(s_1, s_6/2, s_5/2, s_6/2, s_2, s_4/2, s_5/2, s_4/2, s_3)$.
- [15] Y. Le Page, P. Saxe, *Phys. Rev. B* 63 (2001) 174103.
- [16] (a) G. Grimvall, *Thermophysical Properties of Materials*, North-Holland, Amsterdam, 1999;
(b) B.T. Kelly, *Physics of Graphite*, Applied Science, London, 1981.
- [17] O. Beckstein, J.E. Klepeis, G.L.W. Hart, O. Pankratov, *Phys. Rev. B* 63 (2001) 134112.
- [18] W. Zhou, T. Yildirim, *Phys. Rev. B* 74 (2006) 180301(R).